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Cloud Water Chemistry and the Production of Sulfates in Clouds

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16. ABSTRACT

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CLOUD WATER CHEMISTRY AND THE PRODUCTION OF SULFATES IN CLOUDS

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Abstract—Measurements are presented of the pH and ionic content of water collected in clouds over Western Washington and the Los Angeles Basin. Evidence for sulfate production in some of the clouds is presented. Not all of the sulfur in the cloud water was in the form of sulfate. However, the measurements indicate that the production of sulfate in clouds is of considerable significance in the atmosphere. Comparison of field measurements with model results show reasonable agreement and suggest that the production of sulfate in cloud water is a consequence of more than one conversion mechanism.

1. INTRODUCTION

It is becoming apparent that progress in several areas of atmospheric science, (e.g., the global sulfur cycle (Yuen *et al.* 1979), gas-to-particle conversion in the atmosphere (Harrison *et al.* 1975; Barrie and Georgii, 1976; Hegg and Hobbs, 1978), acid rain (Marsh, 1978; Hales, 1978; Hobbs, 1979), and the planetary albedo (Twomey, 1974)), is being retarded by a lack of understanding of the chemistry of clouds.

Most previous field work in this area has been based on the sampling of fogs, mountain-top stratus, and various other clouds that can be sampled from the ground (e.g., Houghton, 1955; Mrose, 1966; Okita, 1968; Lazrus, *et al.* 1970; Falconer and Falconer, 1979). While valuable, it is uncertain how characteristic such sampling is of clouds in the free troposphere. For example, particle size distributions close to the ground are quite different from those in the free troposphere and particle scavenging can influence cloud chemistry.

Most of the airborne studies of cloud chemistry (e.g., Oddie, 1962; Petrenchuk and Drozdova, 1966; Scott, 1978b; Fricke *et al.* 1978) have been conducted outside of the U.S.A. These studies have revealed a considerable range in the pH and ionic content of cloud water. The relationships between these variables and other presumably related parameters (e.g. cloud droplet size distributions, altitude, trace gas concentrations) have not been established. There have been no *direct* measurements reported in the literature on the production of sulfate from SO_2 in clouds.

Attempts to model the chemical processes taking place in clouds have also been rather limited. A chemical model for production of sulfates in liquid water was developed by Scott and Hobbs (1967) and applied to clouds with several simplifying assumptions. Refinements to this model, mainly involving consideration of gas-phase depletion, different aqueous SO_2 oxidation rates and incorporation of cloud condensation nuclei into the cloud water, were made by McKay (1971), Miller and de Pena (1972) and Barrie *et al.* (1974). However, these were all essentially chemical models transferred to some "average" bulk cloud water medium. The first interactive cloud-chemistry model in which chemical reactions were allowed to take place in growing and evaporating cloud droplets, was developed by Easter and Hobbs (1974). This model was recently updated by Hegg and Hobbs (1979) who showed that cloud chemistry can be non-linear, in the sense that bulk cloud water parameters are not always applicable to processes taking place in individual cloud droplets. More recent modeling efforts have tended to concentrate on processes occurring in urban atmospheres and which take place in wetted aerosols rather than cloud droplets (e.g., Middleton *et al.* 1980), or it has been assumed, *a priori*, that liquid-phase oxidation processes are unimportant (Scott, 1978a).

In this paper we present the results of airborne measurements of the ionic composition of cloud water at two locales in the United States, direct measurements of sulfate production in clouds, and comparisons between the sulfate measurements and model predictions.

2. INSTRUMENTATION AND ANALYSIS TECHNIQUES

2.1. *Instrumentation*

All of the field data to be presented were taken aboard the University of Washington's B-23 research aircraft. Most of the instrumentation aboard this aircraft has been described previously (Hobbs *et al.*, 1976; Hobbs *et al.*, 1979; Hegg and Hobbs, 1980). The only instrument that needs some description is the cloud water sampler that we use in warm ($> 0^\circ$ C) clouds. This instrument is a modified version of the aerosol centrifuge described by Scott (1978b). The modifications consist of elimination of the pitched fins on the outer casing (to prevent excessively high rotation rates at high sampling speeds) and the use of differently shaped collection fins on the inner pyramid (for increased sampling efficiency). The outer casing is rotated by means of a small motor at 3400 rpm. At aircraft sampling speeds of $60\,m\,s^{-1}$, only drops with radii $> 3\,\mu m$ were collected. The overall collection efficiency of this cloud water sampler

(i.e. the amount of water actually available for chemical analysis compared to that intercepted by the geometrical cross-section of the sampler) was ~ 10%.

In supercooled (< 0° C) clouds, the chemical analysis was carried out on ice collected on a polyethylene-coated aluminum rod exposed to the airstream from the aircraft. No sampling was done in mixed-phased clouds.

Prior to sampling, the probes of both cloud water samplers were rinsed with distilled, deionized water and dried with Kimwipes. Laboratory tests indicate that such treatment does not affect the pH or ionic content of water subsequently impacted on the probes.

2.2. *Cloud water analysis*

All of the cloud water samples were analyzed for pH and total dissolved sulfur. The pH was measured with a micro-combination pH probe and an expanded-scale pH meter. The sulfur content was determined by means of the flash vaporization technique described by Roberts (1975) and Husar *et al.* (1975). Whenever sample size allowed, analysis was also carried out for various specific anions and cations by means of ion-exchange chromatography (Stevens *et al.*, 1978). Sample handling was as follows. After collection, the samples were sealed in polyethylene containers and maintained at a temperature of 4°C until analysis. The pH of the samples was measured on the ground within three hours of collection. The pH's of selected samples were also analyzed aboard the aircraft within 1 min of collection. The results indicated sample stability within 0.1 pH units over a 3 h period. Flash vaporization and chromatography analysis were generally performed within two days of collection and always within one week of collection; the results of Peden and Skowron (1978) for precipitation indicate sample stability over this time interval.

2.3. *Sulfate production analysis*

Four different techniques were used to estimate the rate of production of sulfate in clouds. Two of these techniques (changes in cloud condensation nucleus spectra and changes in the total particle volume due to cloud passage), and the results obtained from them, have been described elsewhere (Hegg *et al.*, 1981). In this paper we confine our discussion to the other two more direct techniques. The first of these involved determining the particulate sulfate concentrations in the air just upwind and downwind of wave clouds and stationary low-lying stratus clouds.* The samples were collected on filters, the particulate sulfate was then extracted and analyzed either by flash vaporization or ion-exchange chromatography (Husar *et al.*, 1975; Stevens *et al.*, 1978). In the second technique, measurements were made of the sulfate concentrations in cloud water collected at the leading and trailing edges of wave clouds. These concentrations were normalized by the cloud water contents at the two points of measurement in order to allow for the effects of sulfate dilution by water.

* Wave clouds are the lenticular-shaped clouds that commonly form over and downwind of hills where the air is set into an oscillatory motion (see for example, Scorer, 1972). They were chosen because their inflow and outflow regions are relatively well-defined. The stratus clouds had formed over topographic features (e.g. ridges). Care was taken to exclude stratus clouds that might have been subject to "seeding" by ice particles or rain from higher clouds.

3. RESULTS AND DISCUSSION

3.1. *Cloud water data*

Our measurements of cloud water pH and sulfur content are listed in Table 1. The cloud water pH values range from 3.7 to 6.8 with a mean of 5.1 ± 0.9. This range of pH values is in agreement with those reported by other workers. Our mean pH of 5.1 is in agreement with the values previously reported for airborne sampling (Oddie, 1962; Petrenchuk and Drozdova, 1966; Scott, 1978b), but it is somewhat higher than that commonly reported for ground-based sampling (e.g. Falconer and Falconer, 1979). The cloud water sulfur concentrations (expressed as equivalent sulfate concentrations) listed in Table 1 range from 1.5 to 21.9 $mg\,\ell^{-1}$, with a mean value of 11.6 $\pm 6.0\,mg\,\ell^{-1}$. These values are in agreement with the data of Petrenchuk and Drozdova (1966) for cloud water sampled over the U.S.S.R.

The data in Table 1 do not show the strong negative correlation between pH and sulfate concentration found in some rainwater samples (Larson *et al.* 1975; Likens *et al.* 1977). The linear correlation coefficient between our measurements of the pH and sulfate content of cloud water is only 0.17, significant at the 65% level. This lack of significant correlation is also characteristic of the cloud water data reported by Petrenchuk and Drozdova (1966). The correlation coefficient between our measurements of the pH and sulfate concentration of water collected in clouds over the Los Angeles Basin is 0.42, significant at the 80% level. The higher positive correlation for this sub-set of our data is possibly due to the effects of alkaline sea salt, since the air flow was on-shore during the sampling period in the Los Angeles Basin. The correlation coefficient between the pH and sulfate content of the stratus clouds over Western Washington is only −0.11 (significant at less than the 50% level). This suggests that the significant negative correlation between sulfate concentration and pH in rainwater in Western Washington reported by Larson *et al.* (1975) could plausibly be attributed to scavenging below cloud base.

The data in Table 1 do not support Petrenchuk and Drozdova's (1968) hypothesis that clouds with larger droplets have lower ionic concentrations due to dilution. The correlation coefficient between the mean cloud droplet radius and cloud water sulfate for the data listed in Table 1 is only 0.27, significant at the 80% level. It would appear that factors other than dilution

Table 1. Bulk cloud water pH and sulfur measurements in clouds

Date of sample	Mean radius of cloud droplets (μm)	pH	Mass concentration of sulfur (expressed as $SO_4^=$ in mg ℓ^{-1})
	Los Angeles (a) *Stratus clouds*		
10 January 1980	407	4.6	16.5
10 January 1980	10	5.3	1.5
11 January 1980	120	5.3	6.0
10 January 1980	39	5.5	11.1
10 January 1980	1110	5.5	15.3
8 January 1980	11	5.5	19.8
8 January 1980		5.7	21.9
8 January 1980	13	6.6	19.5
8 January 1980	26	6.8	20.4
12 January 1980	57	6.8	16.2
	Western Washington (a) *Stratus clouds*		
30 April 1979	243	3.7	17.8
30 April 1979		3.8	17.9
30 April 1979	105	3.9	12.0
30 April 1979	16	3.9	16.0
3 August 1979	32	3.9	6.4
3 August 1979	32	3.9	4.8
12 July 1979		4.1	19.7
12 July 1979		4.8	14.9
12 July 1979	20	5.2	13.0
12 July 1979	12	5.6	10.9
	(b) *Wave clouds*		
27 April 1979	10.0	4.2	13.2
13 July 1979	3.7	4.3	4.4
24 April 1979	5.4	4.4	7.3
24 April 1979	6.1	4.4	5.5
13 July 1979	3.6	4.5	3.0
3 May 1979		4.6	5.8
3 May 1979	3.1	4.8	9.4
15 May 1979	3.4	5.9	6.3
15 May 1979		5.9	4.8
15 May 1979		5.9	10.0
15 May 1979		6.0	2.5
10 May 1979		6.2	15.7
10 May 1979		6.5	14.7

must be taken into account to explain the observed variations of sulfate concentration in cloud water.

So far we have used the terms sulfur and sulfate somewhat interchangeably. While this is in accord with considerable data that indicates most of the particulate and dissolved sulfur in the atmosphere is sulfate (Stevens *et al.* 1978), it is not necessarily always true. To explore this and other questions, whenever sample size permitted we analyzed the cloud water by ion-exchange chromatography (to determine sulfate concentrations) and flash vaporization (to determine total sulfur). The results are shown in Table 2 and a graphic comparison of the total sulfur and sulfate concentrations is given in Fig. 1. Clearly, not all of the sulfur in cloud water is always in the form of sulfate.

The data listed in Table 2 show the Los Angeles samples to have systematically higher nitrate concentrations than those collected in Western Washington. This is almost certainly an urban–rural contrast. The sulfur data does not show so marked a dichotomy.

Returning to the sulfate concentrations in Table 2, we have previously alluded to the maritime nature of the air sampled in the Los Angeles Basin. The data in Table 2 can be used to determine if the sulfate concentrations in the cloud water over Los Angeles were in excess of those to be expected if the cloud droplets contained only sea salt. This may be done by

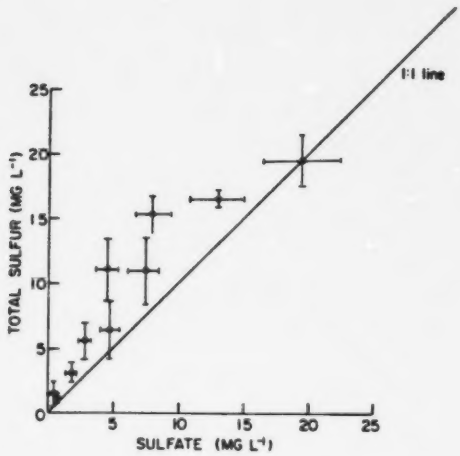

Fig. 1. Comparison of total sulfur concentrations (derived from flash vaporization) with sulfate concentrations (derived by ion-exchange chromatography) for water collected in stratus clouds.

subtracting out the seasalt component of the sulfate by using Na^+ as a tracer of sea salt (e.g. Gravenhorst, 1978). The four samples for which this technique could be applied are listed in Table 3. We see that in these samples there is considerable sulfate in excess of that expected from sea salt. If the concentrations of excess sulfate in the cloud water listed in Table 3 are converted to equivalent clear air particulate sulfate concentrations, they are found to range from 0.02 to 4.8 $\mu g\,m^{-3}$. This range is somewhat lower than that (1–20 $\mu g\,m^{-3}$) found by Hitchcock *et al.* (1980) in their study on the east coast of the United States. Gravenhorst (1978) reported excess sulfate levels of 0.9 $\pm 0.5\,\mu g\,m^{-3}$ in air samples collected over the North Atlantic Ocean.

The excess sulfate in our samples might have been due to either nucleation scavenging of primary, anthropogenic sulfate particles and/or to sulfate production in the cloud droplets. Scott and Laulainen (1979) have recently explored this point by comparing some cloud water sulfate concentrations with sulfate concentrations in the air in which the cloud water nucleated. Unfortunately, the complex air-motions during most of the period of our Los Angeles study generally precluded an unambiguous association of cloud water and clear air sulfate concentrations. However, we do have some data from Western Washington to supplement the few observations taken in Los Angeles and the limited observations of Scott and Laulainen. These data are presented in Table 4. It can be seen that in three out of seven cases the sulfate

Table 2. Concentrations (in $mg\,l^{-1}$) of various chemical species found in cloud water collected in stratus clouds. Gaps indicate no data (due to inadequate sample size for analysis). n.d. indicates species was not detected

Date of sample	Location	pH	[S]*†	$[SO_4^-]$‡	$[NO_3^-]$‡	$[CL^-]$‡	[Na]‡	$[NH_4^+]$‡	$[K^+]$‡
8 January 1980	Los Angeles	6.6	19.5 ± 2.1	19.4	13.8	4.7	5.1	1.9	2.7
10 January 1980	Los Angeles	4.6	16.5 ± 0.6	13.1	12.8	16.0	9.5	4.1	1.8
10 January 1980	Los Angeles	5.5	15.3 ± 1.5	8.1	4.0	27.0			
10 January 1980	Los Angeles	5.3	1.5 ± 0.9§	0.24	n.d.	0.04	0.04	n.d.	0.04
10 January 1980	Los Angeles	5.5	11.1 ± 2.4	4.6	3.0	2.8	2.8	1.0	1.0
11 January 1980	Los Angeles	5.3	6.3 ± 2.1	4.8	3.7	4.3			
12 July 1980	Western Washington	5.6	10.9 ± 2.7	7.3	2.5	n.d.			
12 July 1980	Western Washington	4.2	5.6 ± 1.4	2.9	0.8	n.d.			
12 July 1980	Western Washington	4.4	3.1 ± 0.8	1.8	0.5	n.d.			
12 July 1980	Western Washington	4.1	1.1 ± 0.3	0.7	0.3	n.d.			

* Given in equivalent masses of $SO_4^=$ for comparison with direct $SO_4^=$ measurements.
† Derived from flash vaporization.
‡ Derived from ion-exchange chromatography. Values are accurate to ± 16%.
§ Sample collected over a long time interval including appreciable time spent in relatively high altitude, clean clouds.

Table 3. "Excess" sulfate in cloud water from stratus clouds over the Los Angeles Basin

Date of sample	Liquid water content ($g\,m^{-3}$)	pH	$[SO_4^=]$ ($mg\,l^{-1}$)	[S]* ($mg\,l^{-1}$)	[Tot. Ion]† ($mg\,l^{-1}$)	["Excess" $SO_4^=$]‡ ($mg\,l^{-1}$)
8 January 1980	0.13	6.6	19.4	19.5	47.7	18.1
10 January 1980	0.45	4.6	13.1	16.5	60.7	10.7
10 January 1980	0.6	5.5	4.6	11.1	21.7	3.9
10 January 1980	0.07	5.3	0.24	1.5	1.62	0.23

* Measured by flash vaporization.
† Total measured ion concentration (or "mineralization").
‡ "Excess" $SO_4^=$ is defined as the amount of $SO_4^=$ in the sample in excess of that which can be attributed to scavenging of sea salt.

Table 4. Comparisons of ambient air concentrations of particulate sulfur (expressed as sulfate) measured directly with those derived from measurements of sulfur (also expressed as sulfate) in cloud water

Location	Date of sample	$[SO_4^=]$ Measured directly ($\mu g\ m^{-3}$)	$[SO_4^=]$ Derived from cloud water	pH of cloud water
Western Washington	30 April 1979	1.02	6.20	3.9
Western Washington	3 May 1979	0.93	0.53	4.8
Western Washington	12 July 1979	0.97	30.7	4.8
Western Washington	13 July 1979	0.34	0.19	4.5
Los Angeles	8 January 1980	2.43	2.52	6.6
Los Angeles	8 January 1980	1.92	2.10	5.5
Los Angeles	10 January 1980	1.26	7.50	4.6

concentrations measured directly in the ambient air were significantly lower than those derived from measurements of the sulfate in the cloud water. This suggests that, on occasions, processes other than nucleation scavenging were responsible for the sulfate in the cloud water. In particular, a comparison of the entries in Tables 3 and 4 for the 10 January 1980 sample that has a pH of 4.6 strongly suggests in-cloud sulfate production, since the observed excess in Table 3 cannot be explained by scavenging of particulate sulfate (Table 4). In the three cases for which the sulfate concentrations derived from the cloud water were significantly higher than those measured in the ambient air, the clouds were relatively long-lived stratiform at low altitudes. Petrenchuk and Drozdova also found relatively high sulfate concentrations in such clouds.

3.2. *Sulfate production in clouds*

The results presented in the previous section suggest that under certain conditions sulfate may be produced in clouds. In order to investigate this possibility more directly, we now discuss the measurements in wave clouds.

As explained in Section 2.3, filters were exposed just upwind and downwind of wave clouds and then analyzed for sulfate content. After exposure of the filters, the clouds were penetrated to obtain cloud water samples for pH and aqueous sulfate analysis, and to measure the cloud liquid water contents and droplet spectra. Wind speed, cloud length, and air temperature were also measured. Since it takes considerable time to obtain all these measurements, a wave cloud under study would often evaporate before the measurements were completed. Consequently, our data set is sparse. However, by comparing the experimental results with the interactive cloud-chemistry model of Easter and Hobbs (1974), as updated by Hegg and Hobbs (1979), we are able to gain some insights into sulfate production in cloud droplets.

It should be emphasized at the outset that we have detected sulfate production in only about one-third of the wave clouds we have studied. Whether this is due to a lack of sulfate production in the majority of the clouds or to faulty sampling (e.g., failure to correctly identify the inflow and outflow regions of the cloud) is not known.

The cases where sulfate production was detected are listed in Table 5. Several interesting points are suggested by these results. Firstly, the oxidation rates are generally far higher than those for homogeneous gas-phase oxidation—though they no doubt act over shorter time scales. Secondly, there is a suggestion that the rate of sulfate production increases with the pH of the cloud water. To explore these possibilities in more detail, we now compare predictions of our interactive cloud-chemistry model with the results shown in Table 5.

Shown in Fig. 2 are predictions of the Easter–Hobbs model for sulfate production as a function of time in a

Table 5. Some sulfate production rates measured in wave clouds over Western Washington

Date of sample	Temperature (°K)	Ambient concentrations of ozone (ppb)	Time for sulfate production in the cloud (min)	Ambient concentrations of SO_2 ($\mu g m^{-3}$)*	Cloud water pH	Ambient concentrations of ammonia (ppb)	Production of sulfate in the cloud ($\mu g m^{-3}$)†	Sulfur production rate ($\%h^{-1}$)‡
15 May 1980	266	40	9	7.8	5.9		4.2	300
13 July 1979	263		5.8	7.0	4.4		0.46	70
9 June 1980	274	40	31	14.8	4.3		0.31	4
3 September 1980	258	30	3	5.8	5.1	~1	0.63	200

* These concentrations may be too high, by a factor of 2, due to a problem in zeroing the instrument at high altitudes.
† Downwind concentration of $SO_4^=$ minus the upwind concentration.
‡ Expressed as a percentage of the SO_2 in the ambient air.

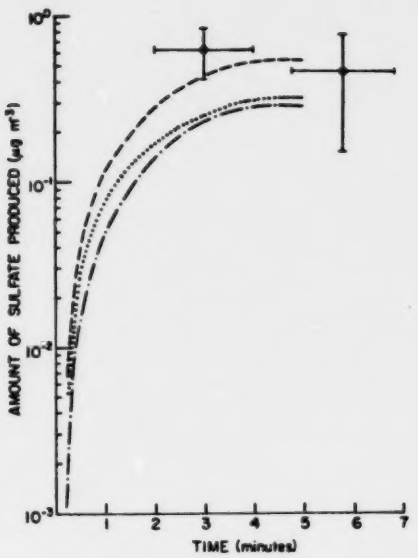

Fig. 2. Comparison of measurements of the amounts of sulfate produced in wave clouds (solid circles with error bars) with the predictions of the Easter and Hobbs (1974) model using various combinations of oxidation rates: Larson *et al.*'s (1978) ($O_2 + O_3$) oxidation rate (dotted line), Larson *et al.*'s (1978) ($O_2 + O_3$) oxidation rate plus Penkett *et al.*'s (1979) H_2O_2 oxidation rate (dashed line), and Brimblecombe and Spedding's (1974) O_2 oxidation rate plus Larson *et al.*'s (1978) O_3 oxidation rate plus Penkett *et al.*'s (1979) H_2O_2 oxidation rate (dashed–dotted line). Concentrations of trace gases inputted into the model were SO_2 = 3 ppb, NH_3 = 1 ppb, O_3 = 50 ppb and H_2O_2 = 0.3 ppb.

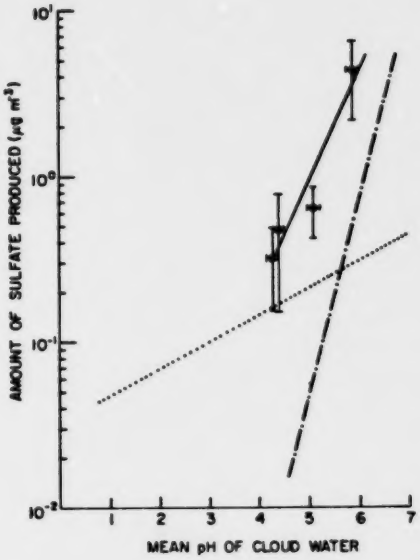

Fig. 3. Comparison of the measured pH dependence of SO_4 production in wave clouds (solid line through four data points) with predictions from the Easter and Hobbs (1974) model using two oxidation rates: Larson *et al.*'s (1978) ($O_2 + O_3$) oxidation rate (dashed–dotted line), Brimblecombe and Spedding's (1974) O_2 oxidation rate plus Larson *et al.*'s O_3 oxidation rate plus Penkett *et al.*'s (1979) H_2O_2 oxidation rate (dotted line).

wave cloud using several plausible combinations of oxidation mechanisms available in the literature. In view of current uncertainties in the rate of uncatalyzed oxidation of aqueous SO_2 by O_2 (Hegg and Hobbs, 1978), two different O_2 oxidation rate expressions have been employed. Because of the strong effects of cloud droplet lifetime and pH on sulfate production (Hegg and Hobbs, 1979), only data points with roughly similar time scales and pH's could be compared to a particular output of the model. Thus only two of the four data points given in Table 5 are shown in Fig. 2. As can be seen in Fig. 2, there is reasonable agreement between the model predictions using the different oxidation rates and our measurements of sulfate productions in wave clouds under similar conditions.

A major uncertainty in the input data for the model was the concentration of H_2O_2, since this species was not measured in our field studies. We have selected a value of 0.3 ppb for this parameter based on reported values for clean air (Kelly *et al.* 1980; Kok, 1980). However, this value could possibly be in error by an order of magnitude. If the H_2O_2 concentrations were on the order of 3 ppb, oxidation by H_2O_2 alone could explain the sulfate productions we measured.

We turn now to the pH dependence of the sulfate production shown in Table 5. Fig. 3 shows the measured pH dependence of the sulfate production compared to that of the model predictions for an $O_2 + O_3$ dominated oxidation rate (dashed-dotted line) and that of an H_2O_2 dominated rate (dotted line). The pH dependence shown by the data is intermediate between those for the $O_2 + O_3$ and H_2O_2 dominated oxidation mechanisms. This suggests that the sulfate production we measured in wave clouds can be explained by a combination of O_2, O_3 and H_2O_2 oxidation within the cloud droplets.

It is interesting to note that the two observations in Table 5 with similar pH's (13 July 1979 and 9 June 1980) suggest that the sulfate production rate falls sharply with increasing time. Such a time dependence has been assumed to be due to the strong pH dependence of most of the mechanisms proposed for sulfate production in clouds (Barrie *et al.*, 1974). This has been well illustrated in the modeling study of Middleton *et al.* (1980) which is applicable to urban air. Under the cleaner conditions examined here, the Easter–Hobbs model also predicts a decrease in the sulfate production rate as a function of time. This is demonstrated in Fig. 4 where the model predictions (for two different combinations of oxidation rates) for sulfate production as a function of time in a relatively large (long through-time) wave cloud are shown. The

amount of sulfate production measured in the June 9 cloud is shown in Fig. 4 for comparison with the model results; we have not included the measurement taken on 13 June 1980 in this figure since simulation of the short cloud through-time for this case would require a different model run.

The model prediction of a fall-off in the sulfate production rate after about 25 min (Fig. 4) is due to evaporation of the cloud droplets at the downwind edge of the wave cloud, and the consequent increase in the concentration of the sulfate in the droplets and the lowering of the droplet pH's. However, between 2 and 25 min, the droplet radii in the cloud are roughly constant and the bending over of the curves during this time interval is due to a lowering of the droplet pH's caused by sulfate production. (In the case of production dominated by H_2O_2, it is also due to H_2O_2 depletion.)

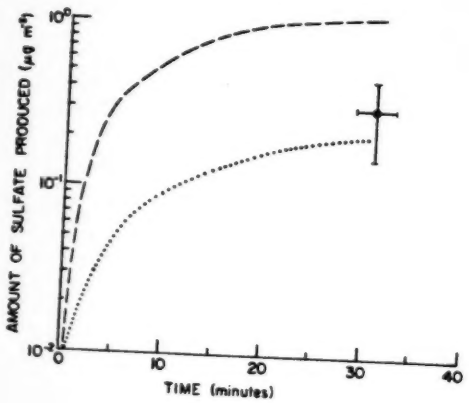

Fig. 4. Predictions of the Easter–Hobbs model for the amount of sulfate produced in a wave cloud as a function of time for two oxidation rates: Larson *et al.*'s (1978) (O_2 + O_3) oxidation rate (dotted line), and Larson *et al.*'s (O_2 + O_3) oxidation rate plus Penkett *et al.*'s (1979) H_2O_2 oxidation rate (dashed line). Concentrations of trace gases inputted into the model were: SO_2 = 3 ppb, NH_3 = 0.1 ppb, O_3 = 50 ppb and H_2O_2 = 0.5 ppb. Also shown (by the solid circle and error bars) is a date point from the measurements in a wave cloud made on 9 June 1980.

It should be emphasized that the concentrations of H_2O_2 and NH_3 used in the model runs shown here are estimates. H_2O_2 concentrations were not measured and the NH_3 levels encountered were generally below the detection limit of our instrument (1 ppb). The NH_3 concentration used in these calculations (0.1 ppb) was chosen to produce a cloud water pH similar to that actually observed on 9 June 1980. The model predicted a mean cloud water pH of 4.6 for the $O_2 + O_3$ run and a pH of 3.9 for the $H_2O_2 + O_2O_3$ run; the measured pH on 9 June was 4.3.

While there is fair agreement between the model predictions and the measurements, the most important point illustrated by Fig. 4 is that aqueous-phase sulfate production can be self-limiting. Therefore, care must be taken in extrapolating rates measured over short times to long time periods, even for relatively clean conditions.

4. SUMMARY AND CONCLUSIONS

Analysis of water samples collected in clouds over Western Washington and the Los Angeles Basin show pH values ranging from 3.7 to 6.8 with a mean of 5.1 ± 0.9 and sulfur concentrations ranging from 1.5 to 21.9 mg ℓ^{-1} with a mean value of 11.6 ± 6.0 mg ℓ^{-1}. Our data suggest that the negative correlation between sulfur concentrations and pH found in rain water is in some cases due to below-cloud scavenging. The negative correlation between sulfur concentration and cloud droplet size suggested by some earlier observations of other workers was not found in our studies. Furthermore, it was found that not all of the sulfur in cloud water was in the form of sulfate. The cloud water samples taken in Los Angeles show evidence of anthropogenic sulfur, however, it is not always clear whether this was primary or secondary sulfur scavenged by the clouds or sulfur produced in the clouds themselves.

Our limited measurements of sulfate production in wave clouds are in reasonable agreement with predictions from the Easter–Hobbs interactive cloud-chemistry model. These comparisons suggest that oxidation by H_2O_2, O_2, and O_3 must all be taken into account in considering aqueous sulfate production in the atmosphere. The results indicate that aqueous sulfate production may be a major source of atmospheric sulfate. However, care should be taken in extrapolating the rates measured over short time periods to long time scales since the sulfate production in cloud droplets appears to be self-limiting.

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